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(54) LITHIUM-NICKEL COMPLEX OXIDE AND ITS PRODUCTION, AND ACTIVE SUBSTANCE OF CATHOD FOR LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a high-purity complex oxide in which each component completely forms a solid solution with LiNiO2 and the cycle characteristics in discharge and charge are improved by adding a lithium compound to a basic metal salt synthesized in the presence of non-oxidizing atmosphere and/or a reducing agent in a water medium, spray-drying or freeze-drying the mixture and baking the mixture under an oxidation atmosphere.

SOLUTION: This complex oxide is represented by formula I [M is Al, Fe, Mn or B; $0.01 \leq (x) \leq 0.5$; $(x)=(x1)+(x2)$; $0.01 \leq (x1) < 0.5$; $0 \leq (x2) < 0.3$; $0.9 \leq (y) \leq 1.3$]. This method for synthesizing the complex oxide comprises adding a lithium compound corresponding to Li atom molar number shown by (y) to a basic metal salt represented by formula II [M is Al, Fe or Mn; An-1 is a n-valent anion; $0.03 < Z < 0.3$; (m) is a positive number] in water medium, adding a boron compound corresponding to atomic number of boron only when boron is included in formula I and subjecting the mixture to spray drying or freeze drying and baking the complex

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CLAIMS

[Claim(s)]
[Claim 1] A general formula [Formula 1] LiyNi1-xCox1Mx2O2 (I)
It is the general formula compounded under a non-oxidizing atmosphere and/or existence of a reducing agent in the manufacture method of the multiple oxide shown by (M shows among a formula at least one or more sorts chosen from aluminum, Fe, Mn, and B group, x is 0.01<=x<=0.5, in x=x1+x2 and x1 0.01 <=x1<0.5 and x2 show 0 <=x2<0.3, and y shows 0.9<=y<=1.3). [Formula 2]
nickel2+1-x(Co2+, Co3+) x1M3+x2(OH)2-nz (An-z) and mH2O (II)
(M shows among a formula at least one or more sorts chosen from aluminum, Fe, and Mn group.) The lithium compound of the amount equivalent to the number of Li atom mols shown in the basic metal salt shown by y is added in water data medium. An- the anion of n ** -- being shown -- Z -- 0.03< Z<0.3 and m -- a positive number -- being shown -- In adding the boron compound equivalent to the atomic number of boron in including boron in the above-mentioned general formula (I), and not including boron, next, as it is The manufacture method of the lithium nickel multiple oxide characterized by spray drying or freeze-drying and subsequently calcinating at about 600 degrees C - 900 degrees C under an oxidizing atmosphere.
[Claim 2] A general formula obtained by making at least one or more sorts of a water-soluble metal salt and the water-soluble alkali salt which are chosen from the inside nickel and Co of a water medium, and aluminum, Fe and Mn group react under a non-oxidizing atmosphere and/or existence of a reducing agent [Formula 3]
nickel2+1-xCo2+x1M3+x2(OH)2-nz (An-z) and mH2O (III)
The manufacture method of the lithium nickel multiple oxide according to claim 1 characterized by coming out and using the basic metal salt shown.
[Claim 3] A manufacture method of a lithium nickel multiple oxide according to claim 1 to 2 that a reducing agent is chosen as an ascorbic acid, a sulfurous acid and thiosulfuric acids or those salts, and a list from sodium borohydride.
[Claim 4] A manufacture method of a lithium nickel multiple oxide according to claim 1 to 3 that an addition of a reducing agent is the 2% or less of the last reaction concentration.
[Claim 5] A manufacture method of a lithium nickel multiple oxide according to claim 1 to 4 characterized by carrying out about 300-500-degree-C preliminary baking under a non-oxidizing atmosphere before calcinating at about 600 degrees C - 900 degrees C under an oxidizing atmosphere.
[Claim 6] Positive active material for lithium secondary batteries which M is at least one or more sorts chosen from aluminum and B group in a general formula (I) of claim 1, and contains a multiple oxide according to claim 1 characterized by for x1 being in 0.01 <=x1<0.5, and x2 being in the range of 0 <=x2<0.3.
[Claim 7] Positive active material for lithium secondary batteries containing a multiple oxide according to claim 1 characterized by for M being shown by aluminum and B, for x1 being in

0.01 <=x1<0.5, and x2 being in the range of 0 <=x2<0.3 in a general formula (I) of claim 1.
[Claim 8] It is characterized by using a basic metal salt shown by the above-mentioned general formula (II) and general formula (III). At least one or more sorts of a water-soluble metal salt and the water-soluble alkali salt which are chosen from the inside nickel and Co of a water medium, and aluminum, Fe and Mn group Supply a reaction vessel with overflow continuously with a metering pump, respectively, make it react to the bottom of stirring by eight or more pH under existence of a reducing agent, lead an overflowing reactant slurry to a thickener, and a slurry condensed with a thickener is used as a seed. Bulk density obtained by returning to a reaction vessel continuously is the manufacture method of about two or more lithium nickel multiple oxides according to claim 1.
[Claim 9] A general formula compounded under a non-oxidizing atmosphere and/or existence of a reducing agent [Formula 4]
nickel2+1-x(Co2+, Co3+) x1M3+x2(OH)2-nz (An-z) and mH2O (II)
(M shows among a formula at least one or more sorts chosen from aluminum, Fe, and Mn group.) The lithium compound of the amount equivalent to the number of Li atom mols shown in the basic metal salt shown by y is added in water data medium. An- the anion of n ** -- being shown -- Next, the following type obtained as it is spray drying or by freeze-drying and subsequently calcinating at about 600 degrees C - 900 degrees C under an oxidizing atmosphere when it adds the boron compound equivalent to the atomic number of boron in including boron in a general formula (I), and it does not include boron [Formula 5] LiyNi1-xCox1Mx2O2 (I)
It is the positive active material for lithium secondary batteries containing the lithium nickel multiple oxide shown by (M shows among a formula at least one or more sorts chosen from aluminum, Fe, Mn, and B group, x is 0.01<=x<=0.5, in x=x1+x2 and x1 0 <=x1<0.5 and x2 show 0 <=x2<0.3, and y shows 0.9<=y<=1.3).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to utilization to the positive active material for lithium secondary batteries at a lithium nickel multiple oxide and its manufacture method list.
[0002]
[Description of the Prior Art] In recent years, it follows on the miniaturization of small electronic equipment, and carrying-ization, and, and it is lightweight to nickel / cadmium cell, and a nickel hydoride battery, and the need of the lithium secondary battery which has high energy density is increasing to them. LiNiO2 and LiCoO2 which are the stratified compound which can intercalate and deintercalate a lithium ion as positive active material of this lithium secondary battery are known. Also in it, from LiCoO2, since it is high electric capacity, LiNiO2 is expected. However, this LiNiO2 has a problem in the cycle property in charge and discharge, and in order to improve the cycle property of this LiNiO2, many attempts which replace and stabilize some nickel of other components (Co, Mn, aluminum, Fe, Ti, V, etc.) are performed. Although the synthetic method of the conventional above LiNiO2 was a process to calcinate after mixing Li components (LiOH, Li2 CO3, LiNO3, etc.), nickel components (a hydroxide, a carbonation object, oxide, etc.), and other components (a hydroxide, a carbonation object, oxide, etc.) by dry type, by this method, that to which the above-mentioned component dissolved thoroughly to nickel is not obtained. Moreover, in order to raise the rate of dissolution, the elevated temperature was needed more, consequently Li might vaporize during baking, and the byproduction of NiO arose and purity lowering might be caused. Therefore, in such a conventional method, while it is difficult to obtain a high grade and the thing to which each component dissolved to LiNiO2 thoroughly, therefore it maintains the high electric capacity which is the feature of LiNiO2, by the time it conquers the badness of the cycle property which is a defect, it will not have resulted.
[0003] In order for this invention persons to replace and do full dissolution of some nickel of LiNiO2 of other components, the basic metal salt which made other components dissolve for a hydroxylation nickel component was compounded, spray drying of the Li was carried out after addition in water data medium, and each component has proposed easily that what carried out full dissolution can be obtained to LiNiO2 by calcinating. Although some nickel was replaced of such other components, and the improvement of the cycle property of LiNiO2 with the extensive thing using Co was found in inside, still, it was not enough. As a result of this invention persons' pursuing a cause further, a part of Co in the dry matter before baking has received oxidation from divalent to trivalent, and, moreover, most of Co3+(OH)3 are not dissolving to nickel (OH)2. Therefore, according to the X diffraction of a burned product, it caught, and although there was no **, most carrier beams Co did not carry out full dissolution of the oxidation LiNiO2 at Co3+, but it was thought owing to it that an improvement of a cycle

property was inadequate and electric capacity was also lower than expected value.
[0004]
[Problem(s) to be Solved by the Invention] This invention aims perfect at providing with the positive active material for lithium secondary batteries the lithium nickel multiple oxide which has improved the high grade, i.e., the cycle property in charge and discharge, and its manufacture method list by each component dissolving LiNiO2. Furthermore, it aims at offering the positive active material for lithium secondary batteries which has improved further storage stability (thermal-protection-system stability at the time of charge) by dissolution of aluminum and/or B, and its manufacture method.
[0005]
[Means for Solving the Problem] this invention persons found out that a lithium nickel multiple oxide obtained by the manufacture method of this invention was useful, as a result of inquiring wholeheartedly, in order to solve the above-mentioned technical problem. That is, this invention is a general formula. [0006]
[Formula 6] LiyNi1-xCox1Mx2O2 (I)
[0007] It is the general formula compounded under a non-oxidizing atmosphere and/or existence of a reducing agent in the manufacture method of the multiple oxide shown by (M shows among a formula at least one or more sorts chosen from aluminum, Fe, Mn, and B group, x is 0.01<=x<=0.5, in x=x1+x2 and x1 0.01 <=x1<0.5 and x2 show 0 <=x2<0.3, and y shows 0.9<=y<=1.3). [0008]
[Formula 7]
nickel2+1-x(Co2+, Co3+) x1M3+x2(OH)2-nz (An-z) and mH2O (II)
[0009] (M shows among a formula at least one or more sorts chosen from aluminum, Fe, and Mn group.) The lithium compound of the amount equivalent to the number of Li atom mols shown in the basic metal salt shown by y is added in water data medium. An- the anion of n ** -- being shown -- Z -- 0.03< Z<0.3 and m -- a positive number -- being shown -- In adding the boron compound equivalent to the atomic number of boron in including boron in the above-mentioned general formula (I), and not including boron, next, as it is It is the manufacture method of the lithium nickel multiple oxide characterized by spray drying or freeze-drying and subsequently calcinating at about 600 degrees C - 900 degrees C under an oxidizing atmosphere. Moreover, before calcinating at about 600 degrees C - 900 degrees C under an oxidizing atmosphere, it is the manufacture method of the lithium nickel multiple oxide characterized by carrying out about 300-500-degree-C preliminary baking under a non-oxidizing atmosphere.
[0010] In case each component compounds the basic metal salt which dissolved to nickel (OH) 2 among water data medium, in order that the point of this invention may suppress oxidation of Co thoroughly, To making a non-oxidizing atmosphere and/or a reducing agent live together, and making them react and a pan, a water-soluble lithium compound or a boron compound is added in water data medium. Spray drying or by freeze-drying It is that obtain the precursor with which Co has not received oxidation in Co3+, and each component obtains easily the lithium nickel multiple oxide which carried out full dissolution LiNiO2 by baking. And it is that the positive active material for lithium secondary batteries with which the cycle property which is the defect of LiNiO2 has fully been improved by the charge and discharge test of a rechargeable battery was obtained.
[0011] As a reducing agent used for this invention, sodium borohydride is raised to an ascorbic acid, a sulfurous acid and thiosulfuric acids or those salts, and a list. A water-soluble reducing agent is suitable for a reducing agent from making it live together during a reaction, for example, an ascorbic acid or its salt is raised as an inorganic system reducing agent as organic system reducing agents, such as a sulfurous acid, thiosulfuric acids, those salts, or sodium borohydride. After baking may remain as an impurity, and although it may be

inconvenience, even if it carries out little survival, especially since an organic system reducing agent vaporizes in a basic metal salt in future baking processes, it is suitable for it, if it remains even when an inorganic system reducing agent is little in the compound basic metal salt.
[0012] Although the amount of the reducing agent used should just be about 2% or less of reaction concentration, it is good to use the minimal dose required for a reaction suitably. In addition, although it is possible to suppress oxidation of Co even if it compounds composition of a basic metal salt only under a non-oxidizing atmosphere, for example, nitrogen, if a still more nearly little reducing agent is made to live together, oxidation will be controlled more nearly thoroughly, and the basic metal salt to which each component dissolved to nickel (OH)2 is obtained.
[0013] Although the synthesis method of the basic metal salt used for the manufacture method of this invention keeps pH or more at about eight and is compounded using a water-soluble metal salt and water-soluble alkali, which method of dropping or dropping of an alkali aqueous solution in a metal salt water solution of a metal salt water solution is sufficient as it at an alkali aqueous solution. Furthermore, precipitate is obtained also by the successive reaction method which trickles simultaneously a metal salt water solution and an alkali aqueous solution, and the basic metal salt which targets this precipitate by filtration and backwashing by water is obtained.
[0014] In order the high multiple oxide of bulk density is required in order to constitute the positive electrode of high capacity, and to obtain the high multiple oxide of this bulk density, a basic metal salt with high ******** is needed. As a synthesis method of a basic metal salt with this high bulk density For example, a metal salt water solution and an alkali aqueous solution are continuously supplied to a reaction vessel with overflow with a metering pump under existence of a reducing agent, respectively. It can be made to be able to react to the bottom of stirring by eight or more pH, the overflowing reactant slurry can be led to a thickener, and bulk density can obtain about two or more basic metal salts by returning to a reaction vessel continuously by using as a seed the slurry condensed with the thickener.
[0015] As a water-soluble metal salt, metal salts, such as nickel, Co, aluminum, Fe, and Mn, are raised, suitably, it chooses from the salts an anion is indicated to be by NO3, SO4, Cl, Br, CH3COO, etc., things can be carried out, and the salt of NO3 and SO4 is more suitably desirable from a reactant field. The amount of the water-soluble metal salt used can be prepared by adjusting a mole ratio and mixing the water-soluble metal salt of each component so that it may become the target presentation.
[0016] As water-soluble alkali, the hydroxide of alkaline metals, a carbonate, a bicarbonate or the carbonate of ammonium, a bicarbonate, etc. are raised. NaOH and Na2CO3 are suitably desirable from a reactant field.
[0017] the basic metal salt used for this invention has a desirable combination of the basic metal salt of NO3- or CO32- from the field whose various profit **** are volatility in future baking reactions as An- of a general formula (II) and (III) by the combination of a water-soluble metal salt and water-soluble alkali.
[0018] As a water-soluble lithium compound added in a basic metal salt, LiOH, LiNO3, Li2CO3, etc. are raised. These one or more sorts can also be used in this invention. Boric acid, lithium tetraborate, etc. are raised as a boron compound.
[0019] In the manufacture method of this invention, the example which uses boric acid as LiOH and a boron compound as a lithium compound is suitable especially from a viewpoint of a cell property from viewpoints, such as a deployment of yield, reactivity, and a resource, and an effect of an oxidation process, as a suitable combination of the above-mentioned compound.
[0020] In the manufacture method of the lithium nickel multiple oxide of this invention, before calcinating at about 600 degrees C - 900 degrees C under an oxidizing atmosphere, it is desirable under a non-oxidizing atmosphere to carry out preliminary baking in an about 300-

500-degree C temperature requirement. Co dissolves to LiNiO2 more certainly and what has the good cell property of the last burned product is obtained by this preliminary baking.
[0021] What is necessary is just to perform baking under an oxidizing atmosphere under oxygen or an air negotiation. Although burning temperature is 600-900 degrees C, it is about 700 - 800 degrees C of abbreviation suitably, and firing time is usually 10 - 45 hours. Burning temperature can be chosen according to the magnitude of the crystal of the multiple oxide of a general formula (I).
[0022] When each component dissolves thoroughly to LiNiO2 and controls oxidation of Co2+ thoroughly especially, the lithium nickel multiple oxide of this invention It is the general formula which the most desirable thing is obtained and is obtained by making at least one or more sorts of the water-soluble metal salt and the water-soluble alkali salt which are chosen from the inside nickel and Co of a water medium, and aluminum, Fe and Mn group react under a non-oxidizing atmosphere and/or existence of a reducing agent as the suitable process. [0023]
[Formula 8]
nickel2+1-xCo2+x1M3+x2(OH)2-nz (An-z) and mH2O (III)
[0024] It can come out and the method using the basic metal salt shown can be raised. Moreover, the positive active material for lithium secondary batteries which contains this multiple oxide as an active principle turned into positive active material which has fully improved the cycle property which is the defect of LiNiO2 in that cell property. Furthermore, it could improve, without spoiling the high electric capacity which is the feature of LiNiO2 about storage stability by making aluminum and/or B dissolve.
[0025] Hereafter, an example explains this invention to details more.
[0026]
[Example]
420ml of sodium-hydroxide solutions of 4.0 mol/l concentration is put into an example 1 sealing reaction container, and nitrogen gas is made full. The aqueous solution of the nickel nitrate of 2.0-mol [/l.] concentration, a cobalt nitrate, and an aluminium nitrate is mixed so that the mole ratio of nickel:Co:aluminum may be set to 8:1:1, and it is dropped over 30 minutes under a room temperature, carrying out the nitrogen gas stream of the 400ml of this mixed aqueous solution. The basic salt slurry of nickel0.8Co0.1aluminum0.1 was obtained by making water suspend the obtained reaction mixture after filtration under nitrogen-gas-atmosphere mind, and rinsing. After making said slurry add 3 mol/l lithium-hydroxide aqueous solution of an amount with which an atomic ratio is equivalent to Li/(nickel+Co+aluminum) =1.05 to (nickel+Co+aluminum) in this slurry, the closed system spray drier which carried out nitrogen fullness performed spray drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 725 degrees C under the oxygen negotiation after 1-hour preliminary baking by 350 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.03nickel0.799Co0.103aluminum 0.097O2.
[0027] 420ml of sodium-hydroxide solutions of 4.0 mol/l concentration is put into an example 2 sealing reaction container, and nitrogen gas is made full. The aqueous solution of the nickel nitrate of 2.0 mol/l concentration, a cobalt nitrate, an aluminium nitrate, and iron nitrate is mixed so that the mole ratio of nickel:Co:aluminum:Fe may be set to 8:1:0.5:0.5, and it is dropped over 30 minutes under a room temperature, carrying out the nitrogen gas stream of the 400ml of this mixed aqueous solution. The basic salt slurry of nickel0.8Co0.1aluminum0.05Fe0.05 was obtained by making water suspend the obtained reaction mixture after filtration under nitrogen-gas-atmosphere mind, and rinsing. After making said slurry add 3 mol/l lithium-hydroxide aqueous solution of an amount with which an atomic ratio is equivalent to Li/(nickel+Co+aluminum+Fe) =1.05 to (nickel+Co+aluminum+Fe) in this slurry, the closed system spray drier which carried out nitrogen fullness performed spray

drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 725 degrees C under the oxygen negotiation after 1-hour preliminary baking by 350 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.04nickel0.799Co0.101aluminum0.048Fe 0.053O2.

[0028] 420ml of sodium-hydroxide solutions of 4.0 mol/l concentration made to dissolve 8.4g of ascorbic acids in an example 3 sealing reaction container is put in, and nitrogen gas is made full. After mixing the aqueous solution of an aluminium nitrate with the nickel nitrate of 2.0 mol/l concentration, and a cobalt nitrate so that the mole ratio of nickel:Co:aluminum may be set to 8:1:1, and dissolving 8g of ascorbic acids in 400ml of this mixed aqueous solution, nitrogen gas is dropped over 30 minutes under a room temperature with a sink. The basic salt slurry of nickel0.8Co0.1aluminum0.1 was obtained by making water suspend the obtained reaction mixture after filtration under nitrogen-gas-atmosphere mind, and rinsing. After the atomic ratio prepared 3 mol/l lithium-hydroxide aqueous solution of the amount equivalent to Li/(nickel+Co+aluminum) =1.05 and made said slurry add to (nickel+Co+aluminum) in this slurry, the closed system spray drier which carried out nitrogen fullness performed spray drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 725 degrees C under the oxygen negotiation after 1-hour preliminary baking by 450 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 45 hours. The chemical composition of a baking object was Li1.03nickel0.802Co0.103aluminum 0.094O2.

[0029] Boric acid was added so that boron might be set to 98:2 by the atomic ratio to (nickel+Co+aluminum) in a slurry at the basic salt slurry of nickel0.8Co0.1aluminum0.1 obtained in the example 4 example 3, and after making 3 mol/l lithium-hydroxide aqueous solution of an amount with which an atomic ratio corresponds further Li/(nickel+Co+aluminum+B) =1.05 add, the closed system spray drier which carried out nitrogen fullness performed spray drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 725 degrees C under the oxygen negotiation after 1-hour preliminary baking by 450 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 45 hours. The chemical composition of a baking object was Li1.04nickel0.785Co0.101aluminum 0.094B0.020O2.

[0030] Na2SO3 was used instead of the ascorbic acid used in the example 5 example 3, it carried out similarly, and the spray drying article was obtained. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 725 degrees C under the oxygen negotiation after 1-hour preliminary baking by 350 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.01nickel0.806Co0.102aluminum 0.093O2.

[0031] The aqueous solution of the nickel sulfate of 2.0 mol/l concentration, cobalt sulfate, and an aluminum sulfate was mixed so that the mole ratio of example 6 nickel:Co:aluminum might be set to 8:1:1, simultaneous adding was performed so that it might become a reaction pH 8.5 about this mixed aqueous solution and the sodium-carbonate aqueous solution of 2.0 mol/l concentration, and the successive reaction was performed in residence-time 20 minutes under the room temperature. The basic salt slurry of nickel0.8Co0.1aluminum0.1 was obtained by making water suspend the obtained reaction mixture after filtration and rinsing. After making said slurry add 3 mol/l lithium-hydroxide aqueous solution of an amount with which an atomic ratio is equivalent to Li/(nickel+Co+aluminum) =1.05 to (nickel+Co+aluminum) in this slurry, the spray drier performed spray drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 750 degrees C under the oxygen negotiation after 1-hour preliminary baking by 450 degrees C under the nitrogen negotiation in the tubular

furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.03nickel0.803Co0.100aluminum 0.097O2.

[0032] Boric acid was added so that boron might be set to 98:2 by the atomic ratio to (nickel+Co+aluminum) in a slurry at the basic salt slurry of nickel0.8Co0.1aluminum0.1 obtained in the example 7 example 6, and after making 3 mol/l lithium-hydroxide aqueous solution of an amount with which an atomic ratio corresponds further Li/ (nickel+Co+aluminum+B) =1.05 add, the spray drier performed spray drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 775 degrees C under the oxygen negotiation after 1-hour preliminary baking by 450 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.04nickel0.786Co0.098aluminum 0.096B0.020O2.

[0033] The aqueous solution of the nickel sulfate of 2.0 mol/l concentration, cobalt sulfate, and an aluminum sulfate is mixed so that the mole ratio of example 8 nickel:Co:aluminum may be set to 8:1:1, and an ascorbic acid is added to this mixed aqueous solution like 1%. The ascorbic acid was dissolved in the sodium-carbonate aqueous solution of 2.0 mol/l concentration like 1%, simultaneous adding was performed so that it might become a sulfuric-acid mixing aqueous solution and a reaction pH 8.5, and the successive reaction was performed in residence-time 20 minutes under the room temperature. The basic salt slurry of nickel0.8Co0.1aluminum0.1 was obtained by making water suspend the obtained reaction mixture after filtration and rinsing. After making said slurry add 3 mol/l lithium-hydroxide aqueous solution of an amount with which an atomic ratio is equivalent to Li/ (nickel+Co+aluminum) =1.05 to (nickel+Co+aluminum) in this slurry, the spray drier performed spray drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 775 degrees C under the oxygen negotiation after 1-hour preliminary baking by 450 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.03nickel0.804Co0.099aluminum 0.097O2.

[0034] The aqueous solution of the nickel nitrate of 2.0 mol/l concentration, a cobalt nitrate, and an aluminium nitrate is mixed so that the mole ratio of example 9 nickel:Co:aluminum may be set to 8:1:1, and an ascorbic acid is added to this mixed aqueous solution like 2%. The ascorbic acid was dissolved in the sodium-hydroxide aqueous solution of 4.0 mol/l concentration like 2%, simultaneous adding was performed so that it might become a nitric-acid mixing aqueous solution and a reaction pH 8.5, and the successive reaction was performed in residence-time 20 minutes under the room temperature. The basic salt slurry of nickel0.8Co0.1aluminum0.1 was obtained by making water suspend the obtained reaction mixture after filtration and rinsing. After making said slurry add 3 mol/l lithium-hydroxide aqueous solution of an amount with which an atomic ratio is equivalent to Li/ (nickel+Co+aluminum) =1.05 to (nickel+Co+aluminum) in this slurry, the spray drier performed spray drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 750 degrees C under the oxygen negotiation after 1-hour preliminary baking by 450 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.03nickel0.799Co0.100aluminum 0.101O2.

[0035] Boric acid was added so that boron might be set to 98:2 by the atomic ratio to (nickel+Co+aluminum) in a slurry at the basic salt slurry of nickel0.8Co0.1aluminum0.1 obtained in the example 10 example 9, and after making 3 mol/l lithium-hydroxide aqueous solution of an amount with which an atomic ratio corresponds further Li/ (nickel+Co+aluminum+B) =1.05 add, the spray drier performed spray drying. The obtained

spray drying article was put into the boat made from an alumina, and it calcinated at 775 degrees C under the oxygen negotiation after 1-hour preliminary baking by 450 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.04nickel0.788Co0.096aluminum 0.096B0.020O2.
[0036] The mixed aqueous solution of the nickel nitrate of 2.0 mol/l, a cobalt nitrate, and an aluminium nitrate was prepared so that the mole ratio of example of comparison 1 nickel:Co:aluminum might be set to 0.8:0.1:0.1, simultaneous adding was performed so that it might become a reaction pH 9.5 about this mixed aqueous solution and the sodium-hydroxide solution of 2.0 mol/l, and the successive reaction was performed in residence-time 20 minutes under the room temperature. The basic salt slurry of nickel0.8Co0.1aluminum0.1 was obtained by making water suspend the obtained reaction mixture after filtration and rinsing. After making said slurry add 3 mol/l lithium-hydroxide aqueous solution of an amount with which an atomic ratio is equivalent to Li/(nickel+Co+aluminum) =1.05 to (nickel+Co+aluminum) in this slurry, the spray drier performed spray drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 725 degrees C under the oxygen negotiation after 1-hour preliminary baking by 350 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.03nickel0.803Co0.100aluminum 0.097O2.
[0037] Boric acid was added so that boron might be set to 98:2 by the atomic ratio to (nickel+Co+aluminum) in a slurry at the basic salt slurry of nickel0.8Co0.1aluminum0.1 obtained in the example 1 of example of comparison 2 comparison, and after making the three-mol [/l.] lithium-hydroxide aqueous solution of an amount with which an atomic ratio corresponds further Li/(nickel+Co+aluminum+B) =1.05 add, the spray drier performed spray drying. The obtained spray drying article was put into the boat made from an alumina, and it calcinated at 750 degrees C under the oxygen negotiation after 1-hour preliminary baking by 450 degrees C under the nitrogen negotiation in the tubular furnace (TF-630 made from the Yamada electrical and electric equipment mold) for 15 hours. The chemical composition of a baking object was Li1.04nickel0.787Co0.098aluminum 0.096B0.019O2.
[0038] Next, whenever [oxidation / of Co of the spray drying article obtained in this example and the example of a comparison] is shown in a table 1. The percentage of trivalent Co to total Co content showed whenever [trivalent / of Co], and it was measured with the oxidation reduction titration. After dissolving 0.2g of samples in the FeSO4-3.6N sulfuric-acid solution of 0.25M and adding 2ml of dark phosphoric acid, it titrates by 0.1-N potassium permanganate. the same -- a blank test -- carrying out -- the following formula -- the total in a sample -- trivalent Co to Co -- it asks for (%) comparatively. For the factor of a 0.1-N potassium permanganate solution, and X0, in a formula, a blank test titration value (ml) and X are [f / the amount of samples (g) and A of a titration value (ml) and m] the contents (%) of Co.
When data showed minus in (%) =58.93f / (X0-X), and mA measurement whenever [trivalent / of Co in a sample], whenever [trivalent / of Co] was displayed as zero.
[0039] The result shown in a table 1 shows that are comparing with the example of a comparison, and oxidation of Co will be thoroughly controlled if oxidation of Co is controlled and a gap also uses especially a reducing agent together for a reaction.
[0040]
[A table 1]

実施例番号	Ｃｏの３価度（%）
実施例１	６．２４
実施例２	６．３２
実施例３	0
実施例４	0
実施例５	0
実施例６	４．４８
実施例７	４．４５
実施例８	0
実施例９	0
実施例１０	0
比較例１	５８．８６
比較例２	５３．８４

[0041] Next, the charge and discharge test of the burned product obtained in this example and the example of a comparison was performed, and assessment of initial capacity and a cycle property was performed. Into the positive-electrode material, it mixed with 6.0 % of the weight of acetylene black as an electric conduction agent 88% of the weight, the lithium nickel multiple oxide obtained in each above-mentioned example was mixed with the mixing ratio of 6.0 % of the weight of tetrafluoroethylenes as a binder, subsequently to a stainless steel mesh top, compression molding was performed into it, and the pellet with a diameter of 18mm was obtained into it. The obtained pellet was dried at 200 degrees C for 2 hours or more, and it considered as the positive-electrode material.
[0042] The porous membrane made from polypropylene (Celgard 2502) and a glass filter-filter paper were used for the diaphragm using what stuck the rolling lithium metal sheet by pressure on the stainless steel base at the negative-electrode material.
[0043] From the assembly of the cel for a trial (half-release mold cel) to finishing was performed all over the dry box which carried out argon substitute using the ethylene carbonate / dimethyl methoxyethane (1:1) which dissolved 1M LiClO4 in the electrolytic solution. Charge and discharge were performed for this lithium cell between 3.0-4.3V by the

constant current density of 0.4 mA/cm2.
[0044] Initial discharge capacity (mAh/g) and the 100th attenuation factor (%) were as being shown in a table 2 as a result of this cell trial. If the manufacturing method of this invention is used as shown in a table 2, the improvement of a cycle property is achieved as compared with the example of a comparison. Although initial capacity does not go up under the effect of a residual reducing agent about an example 5, the cycle property improves.
[0045]
[A table 2]

実施例番号	電池試験 初期容量(mAh/g)	１００回減衰率
実施例１	１６９	６．２
実施例３	１６２	４．９
実施例４	１６５	１．８
実施例５	１１４	０
実施例６	１６０	５．４
実施例７	１７２	１．７
実施例８	１６３	１．９
実施例９	１６５	０．６
実施例１０	１７２	１．７
比較例１	１６５	８．３
比較例２	１６４	９．８

[0046]
[Effect of the Invention] By this invention, a high grade, i.e., the lithium nickel multiple oxide which each component dissolved LiNiO2 thoroughly and has improved the cycle property in charge and discharge, and its manufacture method list were able to be provided with the positive active material for lithium secondary batteries. Furthermore, the positive active material for lithium secondary batteries which has improved further storage stability (thermal-protection-system stability at the time of charge) by dissolution of aluminum and/or B, and its manufacture method have been offered. In case the basic metal salt slurry to which each component dissolved is compounded under water by the process of this invention, in order to suppress oxidation of Co thoroughly, The water-soluble lithium compound or the boron

compound was further added in water data medium, making a non-oxidizing atmosphere and/or a reducing agent living together, and making them reacting and the precursor with which Co has not received oxidation spray drying or by freeze-drying were obtained, and the method of manufacturing the lithium nickel multiple oxide with which each component dissolved thoroughly to LiNiO2 easily by baking has been offered. Moreover, compared with conventional LiNiO2, it is fully improved and the rechargeable battery using the multiple oxide obtained by this process as positive active material for lithium secondary batteries has a useful cycle property on industry.

[Translation done.]